PLASMA PROCESSING METHOD

BACKGROUND OF THE INVENTION

The present invention relates to a plasma processing

5   method for use in a fabrication process of semiconductor de-

vices, and more particularly relates to a plasma processing

method, by which an etching or deposition process is carried

out using plasma created from fluorocarbon gas.

In recent years, downsizing of semiconductor devices has

10   accelerated so much that the required pattern definition is

on the verge of reaching the 0.1μm order at last.

However, the fabrication process of semiconductor de-

vices is basically no different from what it used to be.

That is to say, first, a thin film is deposited on a semicon-

15   ductor substrate. Next, a resist film (i.e., an organic film)

is defined on the thin film by a photolithographic process.

And then the thin film is etched using the resist film.

Nevertheless, the type of exposing radiation, typically

adopted in a lithographic process, has lately changed from i-

20   line into KrF or ArF excimer laser radiation to cope with the

accelerating downsizing trend of semiconductor devices.   In

addition, organic resist films have also been developed re-

sponsive to the change of exposing radiation.

The application of the ArF excimer laser radiation as

25   exposing radiation to the 0.1μm-order patterning is now un-

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der research and development. However, it is known that an organic resist film would be poorly resistant to an etching process in that case.

Thus, to ensure a high selectivity with respect to the resist film, various techniques have been proposed. For example, a technique takes advantage of a property of a silicon material as a fluorine scavenger by making a member inside a reaction chamber out of the silicon material. That is to say, according to the technique, the selectivity against the resist film can be improved by decreasing the concentration of fluorine in an etching gas.

Hereinafter, a known plasma processing method will be described with reference to Figure 1.

Figure 1 illustrates a schematic construction of an inductively coupled plasma processing system. As shown in Figure 1, the inner walls of a reaction chamber 10 are covered with quartz plates 11. An induction coil 12 is wound around the outside of the reaction chamber 10. One end of the induction coil 12 is connected to a first RF power supply 13, while the other end of the induction coil 12 is grounded.

A gas inlet port 14 of the reaction chamber 10 is connected to a gas supply source (i.e., gas cylinder) 16 via a mass flow controller 15. A gas outlet port 17 of the reaction chamber 10 is connected to an exhaust pump 19 by way of a pressure control valve 18. Accordingly, the gas pressure in-

side the reaction chamber **10** is controlled using the mass flow controller **15** and/or the pressure control valve **18** and exhaust pump **19**.

A sample stage **20**, which will be a lower electrode, is provided inside the reaction chamber **10** and connected to a second RF power supply **22** by way of a matching circuit **21**.

A control unit **23** provides control signals to the first and second RF power supplies **12** and **22**, mass flow controller **15** and pressure control valve **18**. In this manner, the unit **23** controls first RF power supplied from the first RF power supply **12** to the induction coil **12**, second RF power supplied from the second RF power supply **22** to the sample stage **22**, the flow rate of the gas supplied from the gas supply source **16** to the reaction chamber **10** and that of the gas exhausted from the reaction chamber **10**.

The gas pressure inside the reaction chamber **10** is normally controlled to a predetermined value between 0.133 and 1.33 Pa by adjusting the pressure control valve **18** with the exhaust pump **19** operated continuously.

The first RF power is applied from the first RF power supply **13** to the induction coil **12** with a process gas supplied through the gas inlet port **14** into the reaction chamber **10** and with the gas pressure inside the reaction chamber **10** kept at the predetermined value. In this manner, plasma is created from the process gas. Thereafter, the second RF pow-

er is applied from the second RF power supply **22** to the sample stage **20**, thereby getting the created plasma attracted to a semiconductor substrate that has been placed on the sample stage **20**. As a result, a thin film, which has been formed on the surface of the semiconductor substrate, is etched or a thin film is deposited on the surface of the semiconductor substrate.

As described above, a silicon material functions as a fluorine scavenger. Accordingly, if an etching gas containing fluorine is introduced into the reaction chamber **10**, then silicon, which is the material of the sample stage **20** and a silicon ring (not shown), combines with that fluorine to produce SiF_x (where $x = 3$ or 4). In this manner, the concentration of fluorine in the etching gas is adjustable and therefore the etch rate is controllable. It is well known that the concentration of fluorine affects the etch rate of a resist film.

Thus, Japanese Laid-Open Publication No. 10-98024 suggests that a fluorocarbon gas, in which the ratio of carbon to fluorine (which will be herein called a "C/F ratio") is relatively high (e.g., C_5F_8 gas), is preferably used to increase the selectivity of a silicon dioxide film being dry-etched (or plasma-etched) to a resist film used as a mask.

However, when the present inventors dry-etched a silicon dioxide film using the C_5F_8 gas with a high C/F ratio and mask-

ing the silicon dioxide film with a resist film, we didn't find that the resultant selectivity increased compared to the conventional C_2F_6 gas with a low C/F ratio.

We carried out the experiment in the following manner.

An ICP plasma-enhanced dry etching system was used as an etching system. The power applied to create plasma was set at 1600 W. A mixture of C_5F_8 and Ar gases was used as an etching gas. The flow rates of the C_5F_8 and Ar gases were defined at 4.7 and 4.0 ml/min, respectively. And the gas pressure was set at 1.33 Pa. A silicon dioxide film was etched using a resist film as a mask under the process conditions such as these.

As a result, although a gas with a high C/F ratio (i.e., the C_5F_8 gas) was used, the selectivity against the resist film was just 1.81, which is not so much different from that of the conventional gas with a low C/F ratio (e.g., C_2F_6 gas).

SUMMARY OF THE INVENTION

In view of these, an object of the present invention is increasing the selectivity attained when dry etching is carried out using a fluorocarbon gas with a C/F ratio of 0.5 or more.

The present inventors believe that if a silicon dioxide film is dry-etched using a fluorocarbon gas with a high C/F ratio, the selectivity thereof to a resist film increases be-

cause of the following reason. Specifically, we believe that a polymer film would be deposited on the surfaces of the silicon dioxide and resist films and decrease the etch rates. Accordingly, if the decrease in etch rate of the silicon di-

5 oxide film is less than the decrease in etch rate of the resist film, then the selectivity to the resist film would increase. On the other hand, if the decrease in etch rate of the silicon dioxide film is equal to or greater than the decrease in etch rate of the resist film, then the selectivity

10 to the resist film would not increase.

Thus, the selectivity to the resist film does not always increase by the use of a fluorocarbon gas with a high C/F ratio. More exactly, the selectivity to the resist film can be increased not only by using the fluorocarbon gas with the

15 high C/F ratio but also by making the etch rate of the silicon dioxide film decrease less than the etch rate of the resist film.

Furthermore, we paid special attention to the residence time τ of the fluorocarbon gas, which is given by $P \times V / Q$,

20 where P is the pressure (unit: Pa) of the fluorocarbon gas, V is the volume (unit: L) of the reaction chamber and Q is the flow rate (unit: Pa $\cdot$ L/sec) of the fluorocarbon gas. By applying numerous combinations of pressures and flow rates of the fluorocarbon gas to reaction chambers with various vol-

25 umes, we tried to find the residence times τ at which the

selectivity to the resist film increases. As a result, we found that where a fluorocarbon gas with a C/F ratio of 0.5 or more was used, the selectivity to the resist film increased if the residence time τ was greater than 0.1 sec and equal to or less than 1 sec. That is to say, we found that the selectivity to the resist film did not increase if the residence time τ was equal to or less than 0.1 sec. This means that the deposition of the polymer film accelerated (i.e., the deposition rate of an organic film increased) in that situation.

As can be seen from the equation for the residence time $\tau = P \times V / Q$, the residence time τ changes with the volume V of the reaction chamber.

Thus, we also found that if $P \times W_0 / Q$, which is a product of the residence time (i.e., $\tau = P \times V / Q$) and the density P_i of power applied to create plasma (i.e., $P_i = W_0 / V$, where W_0 is the magnitude of the power and V is the volume of the reaction chamber), is used, the selectivity to the resist film or the deposition rate of the organic film can be increased irrespective of the volume of the reaction chamber.

The basic idea of the present invention was acquired from these findings. Specifically, the scope of the present invention is defined as follows.

A first inventive plasma processing method includes the steps of: placing a substrate inside a reaction chamber of a

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plasma processing system, a silicon dioxide film having been formed on the surface of the substrate; introducing a fluorocarbon gas, which contains carbon and fluorine and in which a ratio of carbon to fluorine is 0.5 or more, into the reaction chamber; and creating a plasma from the fluorocarbon gas and etching the silicon dioxide film with the plasma. A residence time τ of the fluorocarbon gas in the reaction chamber is controlled at a value greater than 0.1 sec and equal to or less than 1 sec. The residence time τ is given by $P \times V / Q$, where P is a pressure (unit: Pa) of the fluorocarbon gas, V is a volume (unit: L) of the reaction chamber and Q is a flow rate (unit: $Pa \cdot L/sec$) of the fluorocarbon gas.

In the first plasma processing method, the silicon dioxide film is etched with the residence time τ of the fluorocarbon gas in the reaction chamber controlled at a value greater than 0.1 sec and equal to or less than 1 sec. Thus, the selectivity to the resist film can be increased to two or more with the process stabilized.

A second inventive plasma processing method includes the steps of: placing a substrate inside a reaction chamber of a plasma processing system, a silicon dioxide film having been formed on the surface of the substrate; introducing a fluorocarbon gas, which contains carbon and fluorine and in which a ratio of carbon to fluorine is 0.5 or more, into the reaction chamber; and creating a plasma from the fluorocarbon gas and

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etching the silicon dioxide film with the plasma. $P \times W_0 / Q$ is controlled at a value greater than 0.8×10^4 sec $\cdot$ W/m^3 and equal to or less than 8×10^4 sec $\cdot$ W/m^3. $P \times W_0 / Q$ is a product of a residence time τ of the fluorocarbon gas in the reacti-

5 on chamber and a power density Pi of power applied to create the plasma. The residence time τ is given by $P \times V / Q$, where P is a pressure (unit: Pa) of the fluorocarbon gas, V is a volume (unit: L) of the reaction chamber and Q is a flow rate (unit: Pa $\cdot$ L/sec) of the fluorocarbon gas. The power density

10 Pi is given by W_0 / V, where W_0 is a magnitude (unit: W) of the power and V is the volume (unit: L) of the reaction chamber.

In the second plasma processing method, the silicon di-oxide film is etched with $P \times W_0 / Q$, which is a product of a residence time τ of the fluorocarbon gas in the reaction

15 chamber and a power density Pi of power applied to create the plasma, controlled at a value greater than 0.8×10^4 sec $\cdot$ W/m^3 and equal to or less than 8×10^4 sec $\cdot$ W/m^3. Thus, the selec-tivity to the resist film can be increased to two or more with the process stabilized.

20 A third inventive plasma processing method includes the steps of: placing a substrate inside a reaction chamber of a plasma processing system; introducing a fluorocarbon gas, which contains carbon and fluorine and in which a ratio of carbon to fluorine is 0.5 or more, into the reaction chamber;

25 and creating a plasma from the fluorocarbon gas and de-

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positing an organic film on the substrate using the plasma.
A residence time τ of the fluorocarbon gas is controlled at
0.1 sec or less. The residence time τ is given by $P \times V / Q$,
where P is a pressure (unit: Pa) of the fluorocarbon gas, V

5 is a volume (unit: L) of the reaction chamber and Q is a flow
rate (unit: $Pa \cdot L/sec$) of the fluorocarbon gas.

In the third plasma processing method, an organic film
is deposited with the residence time τ of the fluorocarbon
gas in the reaction chamber controlled at 0.1 sec or less.

10 Thus, the deposition rate of the organic film can be in-
creased with the process stabilized.

A fourth inventive plasma processing method includes the
steps of: placing a substrate inside a reaction chamber of a
plasma processing system; introducing a fluorocarbon gas,

15 which contains carbon and fluorine and in which a ratio of
carbon to fluorine is 0.5 or more, into the reaction chamber;
and creating a plasma from the fluorocarbon gas and de-
positing an organic film on the substrate using the plasma.
$P \times W_0 / Q$ is controlled at 0.8×10^4 $sec \cdot W/m^3$ or less. $P \times W_0 / Q$

20 is a product of a residence time τ of the fluorocarbon gas
and a power density Pi of power applied to create the plasma.
The residence time τ is given by $P \times V / Q$, where P is a pres-
sure (unit: Pa) of the fluorocarbon gas, V is a volume (unit:
L) of the reaction chamber and Q is a flow rate (unit: $Pa \cdot$

25 L/sec) of the fluorocarbon gas. The power density Pi is given

by W_0/V, where W_0 is a magnitude (unit: W) of the power and V is the volume (unit: L) of the reaction chamber.

In the fourth plasma processing method, an organic film is deposited with $P \times W_0/Q$, which is a product of a residence time τ of the fluorocarbon gas in the reaction chamber and a power density Pi of power applied to create the plasma, controlled at 0.8×10^4 sec $\cdot$ W/m^3 or less. Thus, the deposition rate of the organic film can be increased with the process stabilized.

In the first through fourth plasma processing methods, the fluorocarbon gas is preferably a gas containing at least one of C_4F_8, C_4F_6, C_3F_8, C_5F_8 and C_6F_6 gases.

In the first through fourth plasma processing methods, the residence time τ is preferably controlled by a mass flow controller provided for the plasma processing system and/or a valve and a pump provided for the plasma processing system.

A fifth inventive plasma processing method includes the steps of: placing a substrate inside a reaction chamber of a plasma processing system, a silicon dioxide film having been formed on the surface of the substrate; introducing a first fluorocarbon gas, which contains carbon and fluorine and in which a ratio of carbon to fluorine is 0.5 or more, into the reaction chamber; creating a first plasma from the first fluorocarbon gas and etching the silicon dioxide film with the first plasma; introducing a second fluorocarbon gas,

which contains carbon and fluorine and in which a ratio of carbon to fluorine is 0.5 or more, into the reaction chamber; and creating a second plasma from the second fluorocarbon gas and depositing an organic film on the etched silicon dioxide film using the second plasma. A first residence time τ_1 of the first fluorocarbon gas in the reaction chamber is controlled at a value greater than 0.1 sec and equal to or less than 1 sec. The first residence time τ_1 is given by $P_1 \times V / Q_1$, where P_1 is a pressure (unit: Pa) of the first fluorocarbon gas, V is a volume (unit: L) of the reaction chamber and Q_1 is a flow rate (unit: Pa·L/sec) of the first fluorocarbon gas. A second residence time τ_2 of the second fluorocarbon gas in the reaction chamber is controlled at 0.1 sec or less. The second residence time τ_2 is given by $P_2 \times V / Q_2$, where P_2 is a pressure (unit: Pa) of the second fluorocarbon gas, V is the volume (unit: L) of the reaction chamber and Q_2 is a flow rate (unit: Pa·L/sec) of the second fluorocarbon gas. In the fifth plasma processing method, the selectivity to the resist film can be increased to two or more and the deposition rate of the organic film can also be increased with the process stabilized.

A sixth inventive plasma processing method includes the steps of: placing a substrate inside a reaction chamber of a plasma processing system, a silicon dioxide film having been formed on the surface of the substrate; introducing a first

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fluorocarbon gas, which contains carbon and fluorine and in which a ratio of carbon to fluorine is 0.5 or more, into the reaction chamber; creating a first plasma from the first fluorocarbon gas and etching the silicon dioxide film with the first plasma; introducing a second fluorocarbon gas, which contains carbon and fluorine and in which a ratio of carbon to fluorine is 0.5 or more, into the reaction chamber; and creating a second plasma from the second fluorocarbon gas and depositing an organic film on the etched silicon dioxide film using the second plasma. $P_1 \times W_1 / Q_1$ is controlled at a value greater than 0.8×10^4 sec $\cdot$ W/m^3 and equal to or less than 8×10^4 sec $\cdot$ W/m^3. $P_1 \times W_1 / Q_1$ is a first product of a first residence time τ_1 of the first fluorocarbon gas in the reaction chamber and a power density Pi_1 of first power applied to create the first plasma. The first residence time τ_1 is given by $P_1 \times V / Q_1$, where P_1 is a pressure (unit: Pa) of the first fluorocarbon gas, V is a volume (unit: L) of the reaction chamber and Q_1 is a flow rate (unit: Pa $\cdot$ L/sec) of the first fluorocarbon gas. The power density Pi_1 is given by W_1/V, where W_1 is a magnitude (unit: W) of the first power and V is the volume (unit: L) of the reaction chamber. And $P_2 \times W_2 / Q_2$ is controlled at 0.8×10^4 sec $\cdot$ W/m^3 or less. $P_2 \times W_2 / Q_2$ is a second product of a second residence time τ_2 of the second fluorocarbon gas in the reaction chamber and a power density Pi_2 of second power applied to create the second

plasma. The second residence time τ_2 is given by $P_2 \times V / Q_2$, where P_2 is a pressure (unit: Pa) of the second fluorocarbon gas, V is the volume (unit: L) of the reaction chamber and Q_2 is a flow rate (unit: Pa·L/sec) of the second fluorocarbon gas. The power density Pi_2 is given by W_2/V, where W_2 is a magnitude (unit: W) of the second power and V is the volume (unit: L) of the reaction chamber.

In the sixth plasma processing method, the selectivity to the resist film can be increased to two or more and the deposition rate of the organic film can also be increased with the process stabilized.

In the fifth or sixth plasma processing method, the first fluorocarbon gas is preferably a gas containing at least one of C_4F_8, C_3F_8, C_5F_8 and C_6F_6 gases, while the second fluorocarbon gas is preferably a gas containing at least one of C_4F_8, C_4F_6, C_3F_8, C_5F_8 and C_6F_6 gases.

In the fifth or sixth plasma processing method, each of the first and second residence times τ_1 and τ_2 is preferably controlled by a mass flow controller provided for the plasma processing system and/or a valve and a pump provided for the plasma processing system.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic cross-sectional view illustrating an inductively coupled plasma processing system applica-

ble to the plasma processing methods of the prior art and embodiments of the present invention.

Figure **2** illustrates relationships between the residence time and the etch rate of a BPSG or resist film that were obtained in respective plasma etching processes performed with the etching gas changed.

Figure **3** illustrates relationships between the residence time and the selectivity to the resist film that were obtained in respective plasma etching processes performed with the etching gas changed.

Figure **4** illustrates the dependence of various kinds of ions on the residence time where plasma was created from a fluorocarbon gas in an inductively coupled plasma processing system.

Figure **5** illustrates relationships between the product of residence time and power density and the etch rate of a BPSG or resist film that were obtained in respective plasma etching processes performed with the etching gas changed.

Figure **6** illustrates relationships between the product of residence time and power density and the selectivity to the resist film that were obtained in respective plasma etching processes performed with the etching gas changed.

Figure **7** illustrates the dependence of various kinds of ions on the product of residence time and power density where plasma was created from a fluorocarbon gas in an inductively

coupled plasma processing system.

Figures **8(a)**, **8(b)** and **8(c)** illustrate the intensity distributions of electron energy of F^- ions that were measured at residence times of 4.5, 5.2 and 13.5 seconds, respectively.

Figure **9** is a flowchart illustrating a plasma processing method according to a first embodiment.

Figure **10** is a flowchart illustrating a plasma processing method according to a second embodiment.

Figure **11** is a flowchart illustrating a plasma processing method according to a third embodiment.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Hereinafter, the basic principle of the invention will be described before plasma processing methods according to respective embodiments of the present invention are detailed.

The following Tables 1, 2 and 3 illustrate the results of experiments that were carried out to obtain the residence time τ of C_5F_8 gas, which was used as an etching gas, in a reaction chamber where a plasma etching process was performed with the volume of the reaction chamber and the flow rate and pressure of the C_5F_8 gas changed.

[Table 1]

×0.133 Pa

	1	5	10	20	30	40	50	60	80	100
1	1.976	9.881	19.76	39.53	59.29	79.05	98.81	118.6	158.1	197.6
5	0.395	1.976	3.953	7.905	11.86	15.81	19.76	23.72	31.62	39.53
10	0.198	0.988	1.976	3.953	5.929	7.905	9.881	11.86	15.81	19.76
15	0.132	0.659	1.318	2.635	3.953	5.27	6.588	7.905	10.54	13.18
20	0.099	0.494	0.988	1.976	2.964	3.953	4.941	5.929	7.905	9.881
25	0.079	0.395	0.791	1.581	2.372	3.162	3.953	4.743	6.324	7.905
50	0.04	0.198	0.395	0.791	1.186	1.581	1.976	2.372	3.162	3.953
100	0.02	0.099	0.198	0.395	0.593	0.791	0.988	1.186	1.581	1.976
150	0.013	0.066	0.132	0.264	0.395	0.527	0.659	0.791	1.054	1.318
200	0.01	0.049	0.099	0.198	0.296	0.395	0.494	0.593	0.791	0.988

×133.3/79.5

(Pa·L/sec)

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[Table 2]

×0.133 Pa

	1	5	10	20	30	40	50	60	80	100
1	0.791	3.953	7.905	15.81	23.72	31.62	39.53	47.43	63.24	79.05
5	0.158	0.791	1.581	3.162	4.743	6.324	7.905	9.486	12.65	15.81
10	0.079	0.395	0.791	1.581	2.372	3.162	3.953	4.743	6.324	7.905
15	0.053	0.264	0.527	1.054	1.581	2.108	2.635	3.162	4.216	5.27
20	0.04	0.198	0.395	0.791	1.186	1.581	1.976	2.372	3.162	3.953
25	0.032	0.158	0.316	0.632	0.949	1.265	1.581	1.897	2.53	3.162
50	0.016	0.079	0.158	0.316	0.474	0.632	0.791	0.949	1.265	1.581
100	0.008	0.04	0.079	0.158	0.237	0.316	0.395	0.474	0.632	0.791
150	0.005	0.026	0.053	0.105	0.158	0.211	0.264	0.316	0.422	0.527
200	0.004	0.02	0.04	0.079	0.119	0.158	0.198	0.237	0.316	0.395

×133.3/79.5

(Pa·L/sec)

[Table 3]

<div align="right">×0.133 Pa</div>

	1	5	10	20	30	40	50	60	80	100
1	3.953	19.76	39.53	79.05	118.6	158.1	197.6	237.2	316.2	395.3
5	0.791	3.953	7.905	15.81	23.72	31.62	39.53	47.43	63.24	79.05
10	0.395	1.976	3.953	7.905	11.86	15.81	19.76	23.72	31.62	39.53
15	0.264	1.318	2.635	5.27	7.905	10.54	13.18	15.81	21.08	26.35
20	0.198	0.988	1.976	3.953	5.929	7.905	9.881	11.86	15.81	19.76
25	0.158	0.791	1.581	3.162	4.743	6.324	7.905	9.486	12.65	15.81
50	0.079	0.395	0.791	1.581	2.372	3.162	3.953	4.743	6.324	7.905
100	0.04	0.198	0.395	0.791	1.186	1.581	1.976	2.372	3.162	3.953
150	0.026	0.132	0.264	0.527	0.791	1.054	1.318	1.581	2.108	2.635
200	0.02	0.099	0.198	0.395	0.593	0.791	0.988	1.186	1.581	1.976

×133.3/79.5

(Pa · L/sec)

Specifically, Table 1, 2 and 3 show the results obtained for the reaction chambers with volumes of 25, 10 and 50 liters, respectively. The experiments for obtaining the residence times τ were carried out with the flow rate of the gas measured by mL per minute under standard conditions. Thus, according to the conversion rate that a gas flow rate of 79.05 mL per minute under standard conditions is equivalent to 133.3 Pa · L/sec, the flow rate of the C_5F_8 gas is represented by the unit of ×133.3/79.05 Pa · L/sec. Also, the gas pressure was measured by mTorr. Thus, according to the conversion rate that 1 mTorr is equivalent to 0.133 Pa, the pressure of the C_5F_8 gas is represented by the unit of ×0.133 Pa.

The data on the residence time τ of the gas shown in Tables 1, 2 and 3 was obtained by substituting the volume

(unit: L) of the reaction chamber and the flow rate (unit: Pa·L/sec) and pressure (unit: Pa) of the gas for the equation $\tau = P \times V / Q$, where τ is the residence time (unit: sec) of the gas in the reaction chamber, P is the pressure (unit: Pa) of the gas, V is the volume (unit: L) of the reaction chamber and Q is the flow rate (unit: Pa·L/sec) of the gas. In Tables 1, 2 and 3, the residence times, at which the selectivity of the silicon dioxide film to the resist film are two or more, are enclosed with the bold lines.

As can be seen from Tables 1, 2 and 3, in performing a plasma etching process using the C_5F_8 gas as an etching gas, the selectivity of the silicon dioxide film to the resist film can be two or more if the residence time τ is greater than 1.0 sec and equal to or less than 1 sec. Some residence time values τ, which are not included inside the bold lines, fall within the range from 1.0 to 1 sec. However, it is known from the results of experiments that the process will be stabilized at any flow rate and any pressure of the gas inside the bold lines. In Tables 1, 2 and 3, the residence time τ is distributed over a wide range from 0.01 to 395.3 sec. In contrast, the present invention selects a very narrow range of 1.0 to 1 sec. And we found that if the residence time is selected from this very narrow range, the process will be stabilized and the selectivity of the silicon dioxide film to the resist film will become two or more.

If the residence time τ is 0.1 sec or less, the selectivity to the resist film decreases. This means that the deposition of polymers accelerates, i.e., the deposition rate of an organic film increases. Accordingly, by setting the residence time τ of the gas at 0.1 sec or less, the deposition rate of an organic film can be increased.

As can be seen from the equation $\tau = P \times V / Q$, the residence time τ changes with the volume V of the reaction chamber.

Thus, $E = P \times W_0 / Q$, which is a product of a power density Pi of the power applied to create the plasma and the residence time τ, is used. The power density Pi is given by W_0/V, where W_0 is a magnitude (unit: W) of the power and V is the volume (unit: L) of the reaction chamber. Then, the selectivity to the resist film or the deposition rate of the organic film can be increased irrespective of the volume of the reaction chamber.

A residence time τ greater than 1.0 sec and equal to or less than 1 sec corresponds to a product E of the residence time τ and power density Pi, which is greater than 0.8×10^4 sec $\cdot$ W/m^3 and equal to or less than 8×10^4 sec $\cdot$ W/m^3.

Accordingly, if the product E of residence time τ and power density Pi is greater than 0.8×10^4 sec $\cdot$ W/m^3 and equal to or less than 8×10^4 sec $\cdot$ W/m^3, then the process will be stabilized and the selectivity of the silicon dioxide film to

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the resist film will be two or more.

In other words, if the product E of residence time τ and power density Pi is 0.8×10^4 sec $\cdot$ W/m^3 or less, then the deposition rate of the organic film increases.

5   Figure 2 illustrates relationships between the residence time τ and the etch rate of a BPSG (borophosphosilicate glass) or resist film that were obtained in respective plasma etching processes performed with the etching gas changed. In Figure 2, the curve plotted with ★ represents the etch rate
10   of the BPSG film where C_2F_6 gas was used. The curve plotted with ◆ represents the etch rate of the BPSG film where C_4F_8 gas was used. The curve plotted with ● represents the etch rate of the BPSG film where C_5F_8 gas was used. The curve plotted with ☆ represents the etch rate of the resist film
15   where the C_2F_6 gas was used. The curve plotted with ◇ represents the etch rate of the resist film where the C_4F_8 gas was used. And the curve plotted with ○ represents the etch rate of the resist film where the C_5F_8 gas was used.

As can be seen from Figure 2, where the C_4F_8 or C_5F_8 gas
20   is used, the shorter the residence time, the lower the etch rates of the BPSG and resist films. This is probably because a polymer film is deposited on the surface of the BPSG or resist film and inhibits the etching action. As also can be seen from Figure 2, where the C_2F_6 gas is used, the shorter
25   the residence time, the higher the etch rates of the BPSG and

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resist films to the contrary.

Figure 3 illustrates the dependence of the ratio of the etch rate of the BPSG film to that of the resist film, i.e., the selectivity to the resist film, on the residence time τ. In Figure 3, the curves plotted with ★, ◆ and ● represent the selectivities where C_2F_6, C_4F_8 and C_5F_8 gases were used, respectively.

As can be seen from Figure 3, where the C_4F_8 or C_5F_8 gas is used, the shorter the residence time, the higher the selectivity to the resist film. However, where the C_4F_8 gas is used, the selectivity decreases if the residence time is 0.2 sec or less. This is because the decrease in etch rate of the BPSG film exceeds the decrease in etch rate of the resist film. As also can be seen from Figure 3, where the C_2F_6 gas is used, the selectivity hardly depends on the residence time.

Taking these results into consideration, we can confirm that where a fluorocarbon gas with a carbon ratio of 0.5 or more, e.g., C_4F_8 or C_5F_8 gas, is used, the etch selectivity can be increased by controlling the residence time at a value greater than 0.1 sec and equal to or less than 1 sec.

Figure 4 illustrates the dependence of ion quantities of F^-, CF^{3-}, $C_2F_5^-$, $C_5F_7^-$, $C_7F_{11}^-$ and $C_8F_{11}^-$ ions on the residence time where plasma was created from a fluorocarbon gas in an inductively coupled plasma processing system. This measurement

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was carried out by an electron attachment mass spectrometry. Accordingly, the F^- ions were created through the dissociative electron attachment process from all of C_xF_y molecules. The CF^{3-} ions were created through the dissociative electron

5 attachment process from CF_4 molecules. The $C_2F_5^-$ ions were created through the dissociative electron attachment process from C_2F_6 molecules. And the $C_5F_7^-$, $C_7F_{11}^-$ and $C_8F_{11}^-$ ions were created through both a similar dissociative electron attachment process and a non-dissociative electron attachment proc-

10 ess.

As can be seen from Figure **4**, as the residence time is shortened, the lower-order ions such as F^-, CF^{3-} and $C_2F_5^-$ ions decrease, while the higher-order ions such as $C_5F_7^-$, $C_7F_{11}^-$ and $C_8F_{11}^-$ ions increase. In other words, as the residence time

15 is shortened, the lower-order molecules decrease while the higher-order molecules increase. Accordingly, it can be seen that the shorter the residence time, the higher the selectivity to the resist film.

Figure **5** illustrates relationships between the product **E**

20 of residence time τ and power density **Pi** and the etch rate of the BPSG or resist film that were obtained in respective plasma etching processes performed with the etching gas changed. The results shown in Figure **5** were obtained with the power density **Pi** supposed to be 1800 W. In Figure **5**, the

25 curve plotted with ★ represents the etch rate of the BPSG

film where C_2F_6 gas was used. The curve plotted with ◆ rep-
resents the etch rate of the BPSG film where C_4F_8 gas was
used. The curve plotted with ● represents the etch rate of
the BPSG film where C_5F_8 gas was used. The curve plotted
5   with ☆ represents the etch rate of the resist film where the
C_2F_6 gas was used. The curve plotted with ◇ represents the
etch rate of the resist film where the C_4F_8 gas was used. And
the curve plotted with ○ represents the etch rate of the re-
sist film where the C_5F_8 gas was used.

10   As can be seen from Figure 5, where the C_4F_8 or C_5F_8 gas
is used, the smaller the product E of residence time and pow-
er density, the lower the etch rates of the BPSG and resist
films. This is because a relationship similar to the above-
described one between the residence time τ and the etch
15   rates of the BPSG and resist films is also met herein.

Figure 6 illustrates the dependence of the selectivity
to the resist film on the product E of residence time and
power density. The results shown in Figure 6 were obtained
with the power density Pi supposed to be 1800 W. In Figure
20   6, the curves plotted with ★, ◆ and ● represent the selec-
tivities where C_2F_6, C_4F_8 and C_5F_8 gases were used, respec-
tively.

As can be seen from Figure 6, where the C_4F_8 or C_5F_8 gas
is used, the smaller the product E of residence time and pow-
25   er density, the higher the selectivity to the resist film.

This is because a relationship similar to the above-described one between the residence time and the selectivity is also met herein.

Taking these results into consideration, we can confirm that where a fluorocarbon gas with a carbon ratio of 0.5 or more, e.g., C_4F_8 or C_5F_8 gas, is used, the etch selectivity can be increased by controlling the product E of residence time and power density at a value greater than 0.8×10^4 sec $\cdot$ W/m^3 and equal to or less than 8×10^4 sec $\cdot$ W/m^3.

Figure **7** illustrates the dependence of ion quantities of F^-, CF^{3-}, $C_2F_5^-$, $C_5F_7^-$, $C_7F_{11}^-$ and $C_8F_{11}^-$ ions on the product E of residence time and power density where plasma was created from a fluorocarbon gas in an inductively coupled plasma processing system.

As can be seen from Figure **7**, as the product E of residence time and power density is decreased, the lower-order ions such as F^-, CF^{3-} and $C_2F_5^-$ ions decrease, while the higher-order ions such as $C_5F_7^-$, $C_7F_{11}^-$ and $C_8F_{11}^-$ ions increase. That is to say, it can be seen that the selectivity to the resist film can be increased by decreasing the product E of residence time and power density.

Figures **8(a)** through **8(c)** illustrate the intensity distributions of electron energy of F^- ions using the residence time as a parameter. Specifically, Figures **8(a)**, **8(b)** and **8(c)** illustrate the results where the residence time was 4.5,

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5.2 and 13.5 seconds, respectively. These intensity distributions can be obtained for molecules with a known cross section, from which a dissociative fragment is observable.

As can be seen from Figures **8(a)** through **8(c)**, as the residence time increases, the C_2F_6 and C_3F_8 gases increase. This phenomenon is in agreement with the results shown in Figure **3**. That is to say, it can be seen from Figures **8(a)** through **8(c)** that a fluorocarbon gas to be regulated, such as C_2F_6 or C_3F_8 gas, which will have detrimental effect on the environment, can be reduced by shortening the residence time.

Japanese Laid-Open Publication No. 5-259119 proposes a technique of increasing the etch selectivity by shortening the residence time τ using a high-speed exhaust pump. The technique disclosed in Japanese Laid-Open Publication No. 5-259119, specifically, the 51st paragraph, Figure 7 and its associated description, appears to be similar to the present invention.

However, Japanese Laid-Open Publication No. 5-259119 discloses nothing about the etching gas. Rather, a problem to be solved by the subject matter of Japanese Laid-Open Publication No. 5-259119 relates to reducing the effects of a reactant (e.g., CO_2) produced from a wafer by exhausting CO_2 (which is on the right side of a chemical formula: $SiO_2 + CF_x \rightarrow SiF_x + CO_2$) at high speeds.

In contrast, the present invention has nothing to do

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with such a problem. Instead, the present invention consists in the finding that to increase the selectivity of a film to a resist film when the film should be etched using a gas with a high C/F ratio, the residence time τ or the product E of residence time and power density should be set within a predetermined range. Thus, the subject matter of Japanese Laid-Open Publication No. 5-259119, which specifies no etching gases, is definitely different from the present invention, which specifies a fluorocarbon gas with a C/F ratio of 2 or more as the process gas, in the technical concept, structure and effects.

EMBODIMENT 1

Hereinafter, a plasma processing method according to a first embodiment will be described with reference to Figures 1 and 9.

First, in Step SA1, a semiconductor substrate is loaded into the reaction chamber 10 of the plasma processing system and placed on the sample stage 20. In this case, a silicon dioxide film has been formed on the semiconductor substrate and a patterned resist film has been defined on the silicon dioxide film.

Next, in Step SA2, a fluorocarbon gas with a C/F ratio of 0.5 or more, e.g., C_5F_8 gas, is introduced into the reaction chamber 10. In this embodiment, the gas pressure is con-

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trolled at a value between 0.665 and 3.99 Pa, e.g., 1.33 Pa.

Then, in Step **SA3**, the flow rate of the gas is controlled using the mass flow controller **15** such that the residence time τ becomes greater than 0.1 sec and equal to or less than 1 sec in accordance with the equation $\tau = P \times V / Q$, where τ is the residence time (unit: sec) of the gas in the reaction chamber, P is a pressure (unit: Pa) of the gas, V is a volume (unit: L) of the reaction chamber and Q is a flow rate (unit: Pa·L/sec) of the gas.

Subsequently, in Step **SA4**, the first RF power is applied from the first RF power supply **13** to the induction coil **12**, thereby creating plasma from the fluorocarbon gas, e.g., C_5F_8 gas. In this case, if the flow rate of the gas is controlled such that the residence time τ becomes greater than 0.1 sec and equal to or less than 1 sec, then $E = P \times W_0 / Q$, which is the product of a power density **Pi** of the first RF power applied to create the plasma and the residence time τ, will be automatically controlled at a value greater than 0.8×10^4 sec · W/m^3 and equal to or less than 8×10^4 sec · W/m^3. The power density **Pi** is given by W_0/V, where W_0 is a magnitude (unit: W) of the power and V is the volume (unit: L) of the reaction chamber.

Thereafter, in Step **SA5**, the second RF power is applied from the second RF power supply **22** to the sample stage **20**, thereby getting the created plasma attracted to the semicon-

ductor substrate on the sample stage **20**. Finally, in Step **SA6**, the silicon dioxide film is plasma-etched using the resist film as a mask.

According to the first embodiment, the residence time τ of the perfluorocarbon gas in the reaction chamber is set greater than 0.1 sec and equal to or less than 1 sec, and $E = P \times W_0/Q$, which is the product of the power density **Pi** of the first RF power and the residence time τ, is set greater than 0.8×10^4 sec $\cdot$ W/m^3 and equal to or less than 8×10^4 sec $\cdot$ W/m^3. Thus, the selectivity of the silicon dioxide film to the resist film can be increased to two or more.

EMBODIMENT 2

Hereinafter, a plasma processing method according to a second embodiment will be described with reference to Figures 1 and 10.

First, in Step **SB1**, a semiconductor substrate is loaded into the reaction chamber **10** of the plasma processing system and placed on the sample stage **20**.

Next, in Step **SB2**, a fluorocarbon gas with a C/F ratio of 0.5 or more, e.g., C_5F_8 gas, is introduced into the reaction chamber **10**. In this embodiment, the gas pressure is controlled at a value between 0.665 and 3.99 Pa, e.g., 1.33 Pa.

Then, in Step **SB3**, the flow rate of the gas is controlled using the mass flow controller **15** such that the residence time

τ becomes 0.1 sec or less in accordance with the equation $\tau = P \times V / Q$.

Subsequently, in Step **SB4**, the first RF power is applied from the first RF power supply **13** to the induction coil **12**, thereby creating plasma from the fluorocarbon gas, e.g., C_5F_8 gas. In this case, if the flow rate of the gas is controlled such that the residence time τ becomes 0.1 sec or less, then $E = P \times W_0 / Q$, which is the product of a power density **Pi** of the first RF power applied to create the plasma and the residence time τ, will be automatically controlled at 0.8×10^4 sec · W/m^3 or less.

Thereafter, in Step **SB5**, the second RF power is applied from the second RF power supply **22** to the sample stage **20**, thereby getting the created plasma attracted to the semiconductor substrate on the sample stage **20**. Finally, in Step **SA6**, an organic film is deposited on the semiconductor substrate.

According to the second embodiment, the residence time τ of the perfluorocarbon gas in the reaction chamber is set at 0.1 sec or less and $E = P \times W_0 / Q$, which is the product of the power density **Pi** of the first RF power and the residence time τ, is set at 0.8×10^4 sec · W/m^3 or less. Thus, an organic film can be formed at a high deposition rate.

EMBODIMENT 3

Hereinafter, a plasma processing method according to a

third embodiment will be described with reference to Figures 1 and 11.

First, in Step SC1, a semiconductor substrate is loaded into the reaction chamber 10 of the plasma processing system and placed on the sample stage 20.

Next, in Step SC2, a first fluorocarbon gas with a C/F ratio of 0.5 or more, e.g., C_5F_8 gas, is introduced into the reaction chamber 10. In this embodiment, the gas pressure is controlled at a value between 0.665 and 3.99 Pa, e.g., 1.33 Pa.

Then, in Step SC3, the flow rate of the first gas is controlled using the mass flow controller 15 such that the residence time τ becomes greater than 0.1 sec and equal to or less than 1 sec in accordance with the equation $\tau = P \times V / Q$.

Subsequently, in Step SC4, the first RF power is applied from the first RF power supply 13 to the induction coil 12, thereby creating first plasma from the first fluorocarbon gas, e.g., C_5F_8 gas. In this case, if the flow rate of the first gas is controlled such that the residence time τ becomes greater than 0.1 sec and equal to or less than 1 sec, then $E = P \times W_0 / Q$, which is the product of a power density P_i of the first RF power applied to create the first plasma and the residence time τ, will be automatically controlled at a value greater than 0.8×10^4 sec $\cdot$ W/m^3 and equal to or less than 8×10^4 sec $\cdot$ W/m^3.

Thereafter, in Step SC5, the second RF power is applied

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from the second RF power supply **22** to the sample stage **20**, thereby getting the first plasma attracted to the semiconductor substrate on the sample stage **20**. Next, in Step **SC6**, a silicon dioxide film is plasma-etched using a resist film as a mask.

When the plasma etching ends, the supply of the first perfluorocarbon gas is stopped and then oxygen gas is introduced into the reaction chamber **10** in Step **SC7** to create oxygen plasma from the oxygen gas. In this manner, the resist film on the silicon dioxide film is ashed away.

Next, in Step **SC8**, a second fluorocarbon gas with a C/F ratio of 0.5 or more, e.g., C_5F_8 gas, is introduced into the reaction chamber **10**. In this embodiment, the gas pressure is controlled at a value between 0.665 and 3.99 Pa, e.g., 1.33 Pa.

Then, in Step **SC9**, the flow rate of the second gas is controlled using the mass flow controller **15** such that the residence time τ becomes 0.1 sec or less in accordance with the equation $\tau = P \times V / Q$.

Subsequently, in Step **SC10**, the first RF power is applied from the first RF power supply **13** to the induction coil **12**, thereby creating plasma from the second fluorocarbon gas, e.g., C_5F_8 gas. In this case, if the flow rate of the second gas is controlled such that the residence time τ of the gas becomes 0.1 sec or less, then $E = P \times W_0 / Q$, which is the product of a power density **Pi** of the first RF power applied to create

the second plasma and the residence time τ, will be automatically controlled at 0.8×10^4 sec $\cdot$ W/m^3 or less.

Thereafter, in Step **SC11**, the second RF power is applied from the second RF power supply **22** to the sample stage **20**, thereby getting the created plasma attracted to the semiconductor substrate on the sample stage **20**. Finally, in Step **SC12**, an organic film is deposited on the silicon dioxide film.

In the first through third embodiments, C_5F_8 gas is used by itself as the fluorocarbon gas. Alternatively, C_4F_8, C_4F_6, C_3F_8 or C_6F_6 gas may be used by itself or a mixture thereof may also be used.

In the third embodiment, the same gas is used as the first and second fluorocarbon gases. However, the first and second fluorocarbon gases may be either the same or different from each other.

Also, in the first through third embodiments, an inductively coupled plasma processing system is used as an exemplary plasma processing system. Alternatively, an ECR plasma processing system or surface wave excited plasma processing system may also be used.

Furthermore, in the first through third embodiments, the flow rate of the gas is controlled using the mass flow controller **15**. However, the flow rate is controllable using the mass flow controller **15** and/or the pressure control valve **18** and the exhaust pump **19**. Moreover, the flow rate of the

fluorocarbon gas may also be controlled not only by mixing the process gas with inert gas, nitrogen gas, carbon monoxide gas or carbon dioxide gas but also by adjusting the flow rates of these gases.